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13. ABSTRACT (Maximum 200 words)

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Plans for the next period of performance are to accurately measure group III and V sticking coefficients versus temperature and compare with growth theories.

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Annual Technical Report

Year 2
July,1 1990 - June 30, 1991

Growth Studies of CVD-MBE by In-situ Diagnostics

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Abstract

This is a progress report for the second year of the DARPA - URI program "Growth Studies of CVD-MBE by in-situ Diagnostics." The goals of the program are to develop non-invasive, real time epitaxial growth monitoring techniques and combine them to gain an understanding of processes that occur during MBE growth from gas sources. We have adapted these techniques to a commercially designed gas source MBE system (Vacuum Generators Inc.) to facilitate technology transfer out of the laboratory into industrial environments.

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Plans for the next period of performance are to accurately measure group III and V sticking coefficients versus temperature and compare with growth theories.

Introduction

During the first year of the DARPA-URI program, effort was directed almost exclusively toward hardware and software development of in-situ MBE growth monitoring techniques and hydride cracker design. We have successfully redesigned our hydride cracker [1] for improved cracking efficiency and flux uniformity. A number of prototype systems were constructed for spectroscopic ellipsometry (SE) and laser induced fluorescence (LIF) which had the capability of being adapted to a commercial MBE system. A collaboration with the J.A. Woolam Co. (who is a DARPA contractor) in spectroscopic ellipsometry was established and resulted in the present SE system. The goals of this time period were to obtain a capability with which the growth of semiconductor surfaces could be monitored by three complementary techniques having submonolayer sensitivity and time resolution on the order of constituent surface migration times. We have been successful in these goals and have achieved a unique facility with which to monitor optical, chemical and structural properties of the growing surface in an MBE having gaseous sources.

In the second year we continued to identify technical aspects of in-situ characterization specific to the growth monitoring application and have refined our systems to the point where we have measured several important growth parameters. Our concentration, however, was to use the techniques to obtain relevant parameters for use in growth models. This progress is described in the body of this report.

At the end of year 1, one of the program investigators left Arizona State University. Professor K.K. Bajaj accepted a position at Emory University as Chair of the Physics Department and is no longer collaborating on the Monte Carlo simulations. We have thus altered the theoretical direction of the program slightly and adopted a kinetics model approach which will provide the experimental program insight in a shorter time with the data available to us.

The progress under this research program has led to several major developments. The developments are in the areas of in-situ measurement development and implementation, improved growth resulting from the information gleaned from the data and measurement of properties not possible before. The main points are itemized here and discussed later in this section.

* In conjunction with the J.A. Woolam Co. we have developed an in-situ spectroscopic ellipsometry system that is compatible with both MBE and MOCVD reactors. The prototypes resulting from the joint collaboration have resulted in a commercial product that is the most flexible and advanced available to date.
* We have used SE to measure the MBE substrate temperature from room temperature to typical growth temperatures. This is a major extension over conventional measurement techniques (optical pyrometry) which accurately determine temperature only above 400°C.
* We have been the first to track the growth of an MBE multiple quantum well by SE.
* We have constructed a laser induced fluorescence system and adapted it to a commercial MBE system for monitoring of MBE growth processes. Atomic group III and dimeric As_2 and P_2 have been identified and characterized.
* Thermal desorption properties of P_2 on InP substrates have been quantified by LIF.
* We have used the techniques to grow GaAs/AlGaAs quantum wells in GSMBE with record narrow luminescence linewidths of 0.6 meV at 2K for a 100Å well.

In the next period of performance, we plan to quantify sticking coefficients, reaction rates and monitor diatomic species as a function of growth temperature and incident flux. These parameters can then be used in our and other researchers' models in attempts to understand growth at semiconductor surfaces.

Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) is based on measuring the polarization state of reflected light, at multiple wavelengths, when linearly polarized light is made incident on a sample. This is achieved by determining a complex reflection coefficient ratio ρ of the sample, which in turn is defined as the quotient of the complex reflection coefficients for light polarized parallel (R_p) and perpendicular (R_s) to the plane of incidence. In the simplest case of the two-phase model which consists of ambient (air or vacuum) / substrate with no additional layers, $R_{p, s}$ represent the Fresnel reflection coefficients of the system. Usually, ρ is transformed into the "ellipsometric parameters" Ψ and Δ, which characterize the polarization state of the reflected light according to the relation:

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta}, \qquad (1)$$

where $\tan(\Psi)$ is the amplitude and Δ is the phase difference between the two components of the electric field. The SE experimental measurements are expressed as $\Psi(hv_i, \Phi_j)$ and $\Delta(hv_i, \Phi_j)$ where hv_i is the photon energy and Φ_j is the external angle of incidence. The measured ellipsometric parameters, Ψ and Δ, are sensitive to the structure (layer thicknesses, compositions, microstructure, etc.) and the optical constants of the sample. In addition, SE is sensitive to any physical property or process which affects the optical constants and/or surface or interface conditions: i.e. for example temperature.

To extract surface temperature by SE, it is necessary to known a priori the temperature dependent optical constants [4] for the particular material studied. The range in which the temperature can be measured is limited to the range over which the optical constants are known. The determination of temperature dependent optical constants for GaAs has only recently been achieved by Yao, Snyder, and Woollam [5]. These pseudo-optical constants [5] of GaAs serve as a set of reference functions, which we have used to find unknown sample surface temperatures by fitting the measured data.

The concept of using ellipsometry to measure the surface temperature of a Si substrate in a UHV setting was first suggested by Ibrahim and Bashara in 1972 [2]. Tomita et al [3], in 1986, also proposed the use of ellipsometry to measure the surface temperature of Si and GaAs. We have successfully implemented this on our MBE system. We have found [6] (see figure 1) that the surface temperature in MBE can differ by more than 150°C from that measured by the thermocouple. Furthermore, using SE, we have extended the temperature measurement range down to room temperature from the optical pyrometer limit of approximately 450°C. The measurement of surface temperature is extremely important in surface growth kinetics studies because of the inherently exponential temperature dependence of the reactions. With this technique, much of the ambiguity in interpreting sticking coefficients arising from errors in temperature measurement can be eliminated. We plan to refine this technique to increase the accuracy of the temperature determination.

● ELLIPSOMETER TEMPERATURE

---- VG-ellips

○ PYROMETER TEMPERATURE

▲ VG thermocouple

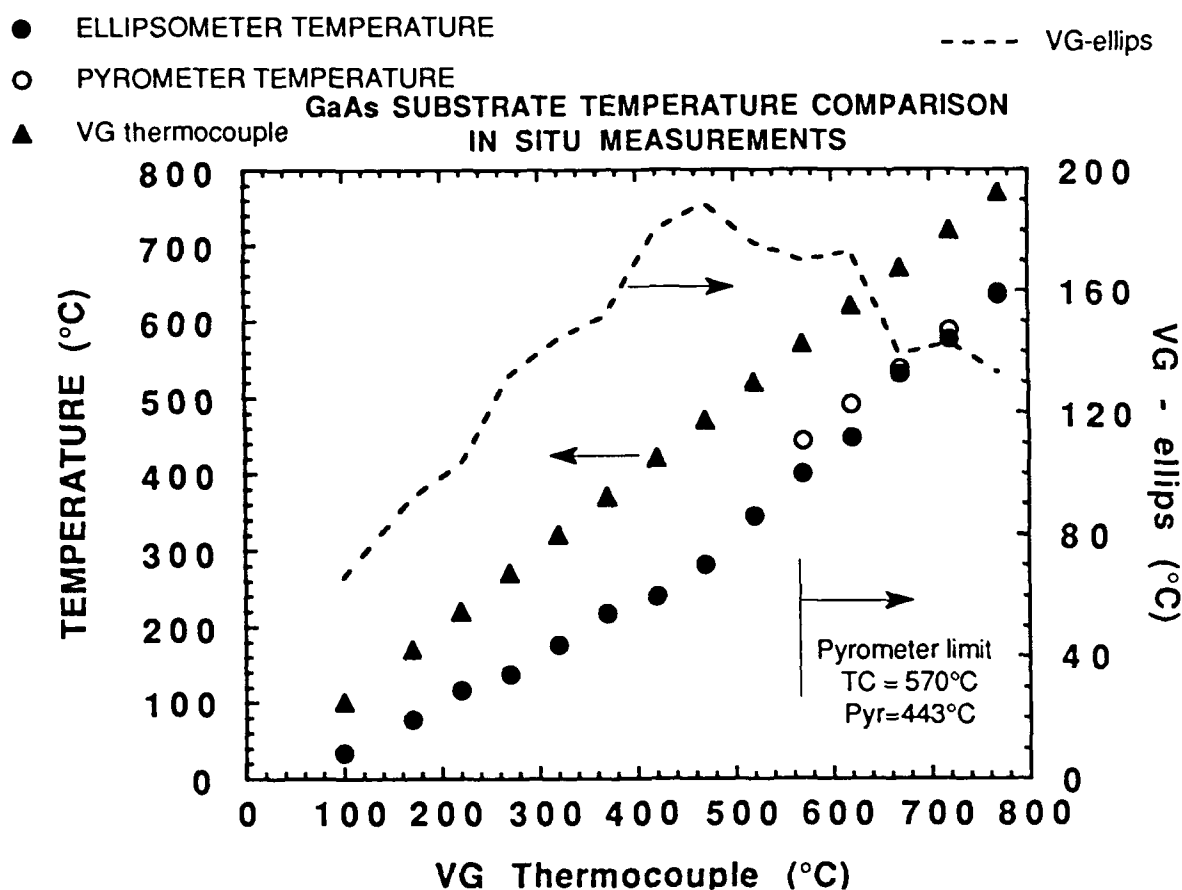GaAs SUBSTRATE TEMPERATURE COMPARISON
IN SITU MEASUREMENTS

Figure 1   A comparison of substrate temperature determined by thermocouple, optical pyrometer and spectroscopic ellipsometer. The difference between the thermocouple and ellipsometer is plotted on the axis to the right. It should be noted that the ellipsometer can measure temperatures from typical growth temperatures to room temperature.

Another consideration for studying epitaxial growth kinetics is the condition of the surface that is to be grown on. Often RHEED does not provide information on surface porosity (for example). Illustrated in figure 2 is a real-time ellipsometric trace of a typical growth run consisting of GaAs oxide desorption, substrate annealing, surface smoothing by a Ga pulse, the growth of 2000Å of $Al_{0.25}Ga_{0.75}As$ and a 500Å GaAs cap. The substrate is ramped to the appropriate temperatures required for growth of each layer. A gradual change of the optical properties of the native oxide is observed before the catastrophic "blow-off" is observed by RHEED. Aspnes [8] assumed a surface roughening model to describe such an effect. It is likely that a combination of surface roughening and a change of oxide composition (or optical constants) is occurring. We would like to obtain an independent measure of the change in oxide chemistry to confirm this hypothesis. No change is observed by RHEED during the anneal stage but a slight change is seen by SE. It should be noted that surface changes are

observed even at the relatively long wavelength of 5000Å. As the wavelength is decreased, the measurement becomes more surface sensitive and, in fact, monolayer changes in surface have been observed [7] by our group. An example of this is shown in figure 3 which plots psi at 3000Å versus time after the Ga smoothing pulse indicated in figure 2. An exponential fit to the data is also shown indicating that after the Ga pulse occurs the surface stabilizes with a time constant of approximately 80 seconds at this substrate temperature.

PSI VS. TIME AT A WAVELENGTH OF 500nm
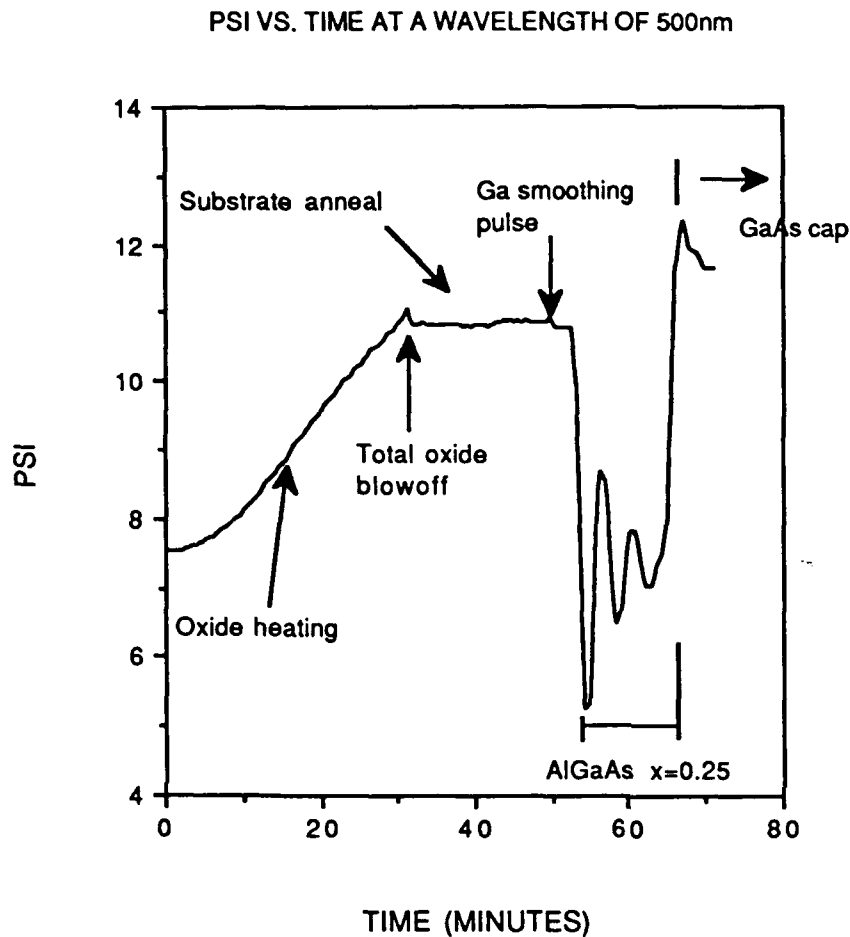

TIME (MINUTES)

Figure 2   Real-time monitoring by of the growth of a thick (2500Å) AlGaAs epitaxial layer on a GaAs substrate. This curve was taken at a wavelength of 5000Å.

Thus we demonstrate the capability of using in situ SE to monitor surface changes on the order of one monolayer in thickness.
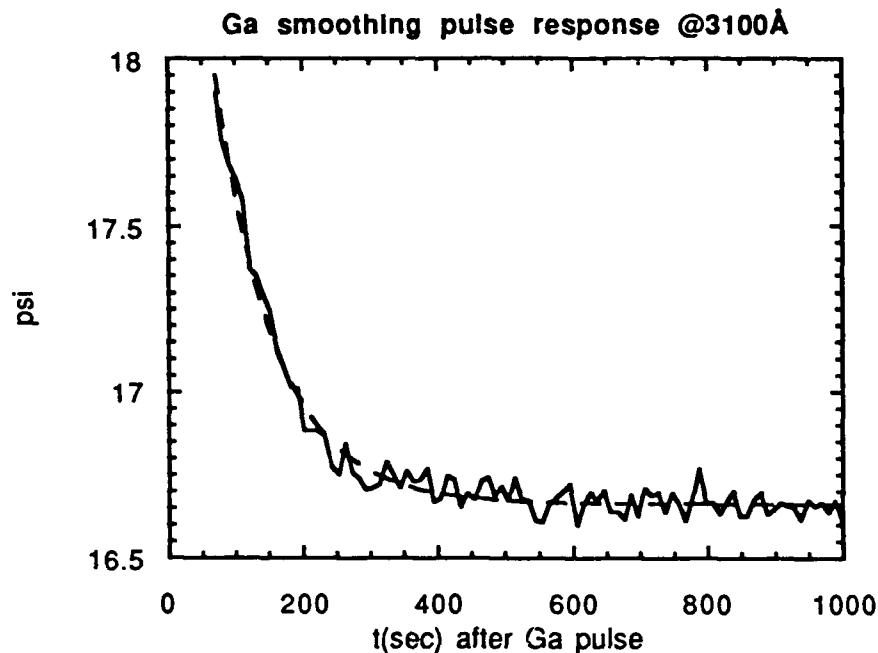
Ga smoothing pulse response @3100Å

Figure 3   At higher time resolution, the behavior of psi is measured after the Ga
smoothing pulse is turned off. The data (solid line) is fit with an exponential (dashed line) yielding a time constant
of approximately 80 seconds.

The corresponding Ψ versus Δ, or velocity plot, of this growth run is shown in figure 4. The trajectory
converges to three main points corresponding to the optical constants of the optically thick native oxide, GaAs and
AlGaAs. When the real and imaginary parts of the dielectric constant are plotted as in figure 4, the position of the
locus is an indication of the alloy composition of the epitaxial layer. Aspnes [8] has used this to control aluminum
composition in a CBE system. Consequently, the alloy composition of the film can be determined during growth
and also after growth is terminated. Each point represents a multiple wavelength spectroscopic scan. For fast
surface processes, a scan at a single wavelength can be performed which can resolve features occurring in the
several hundred millisecond time scale.

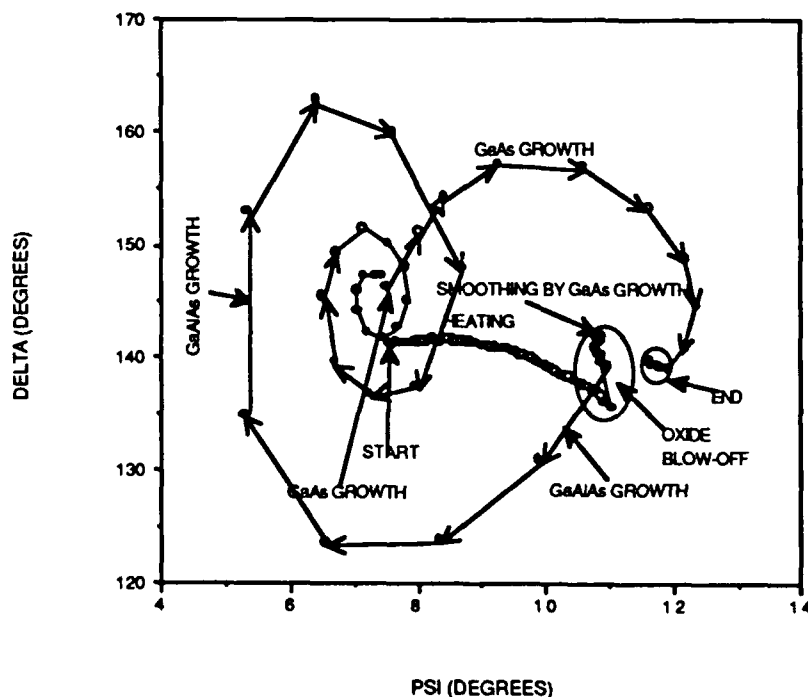VELOCITY PLOTS OF THE DELTA PSI TRAJECTORIES AT A WAVELENGTH OF 500nm

Figure 4   The velocity plot corresponding to the growth run shown in figure 2 shows the spiraling of the trajectory to the optically thick values of GaAs and AlGaAs at the wavelength of 5000Å.

For the growth of quantum wells and superlattices a high degree of interface smoothness is required. Thus a non-invasive real-time monitor of the growth conditions required for interface smoothness [7] is essential. We have the capability to take approximately ten ellipsometric data points per second which, at a growth rate of one monolayer per second, can provide sufficient resolution to monitor this parameter. Proof of this is in figure 5 in which we show the growth of GaAs/AlGaAs multiple quantum wells. The wells are 100Å wide while the barriers are 200Å. We are in the process of explaining the observed behavior.

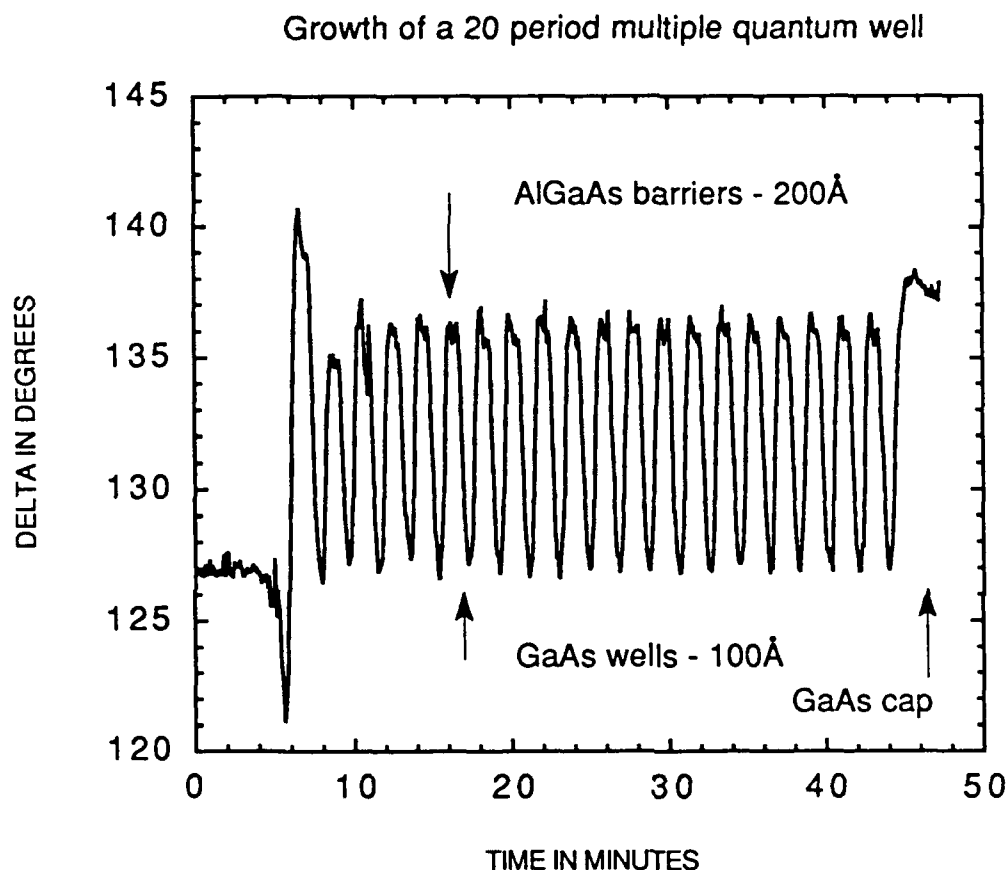## Growth of a 20 period multiple quantum well

Figure 5   Ellipsometric tracking of the growth of a 20 period MBE AlGaAs/GaAs multiple quantum well.

In summary we have shown that in-situ ellipsometry can be used to study:
* changes in the semiconductor growth surface of approximately one monolayer
* the substrate surface temperature from room temperature to typical growth temperatures
* the evolution of growth in a multilayered structure
* interface roughness

These parameters are essential to complement the chemical and structural investigations and also to provide accurate values for growth models. In addition to the basic properties study, we have used the techniques described here to obtain record narrow photoluminescence linewidths [9] in GSMBE GaAs/AlGaAs quantum wells of 0.6 meV for a width of 100Å (see figure 6). Optimization of substrate temperature and growth interruption time were used to obtain these results. Figure 7 shows the best reported linewidths obtained with different growth techniques including ours.
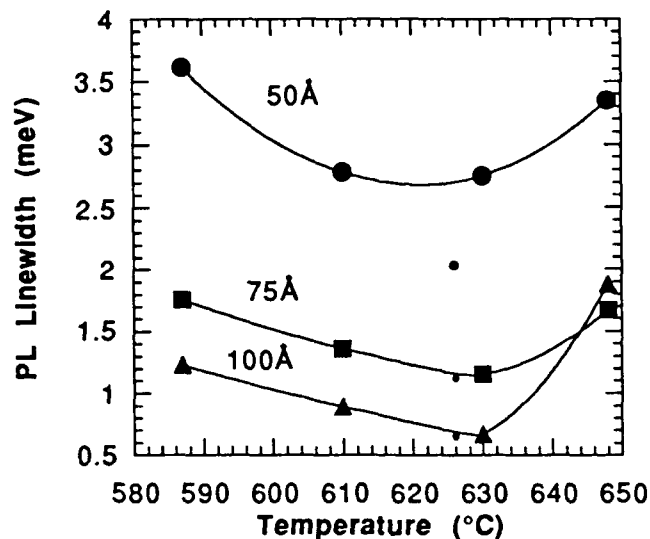
Figure 6   2K PL linewidths are plotted for 50Å, 75Å and 100Å GaAs/ AlGaAs QWs grown at different
substrate temperatures. All QWs were grown with only one interrupt at the normal interface except for the QWs
grown at 626°C which had interrupts both at the normal and inverted interfaces. The 2K PL linewidth for the 100Å
GSMBE well is 0.62 meV which is the narrowest reported for GSMBE. The best linewidth obtained by solid source
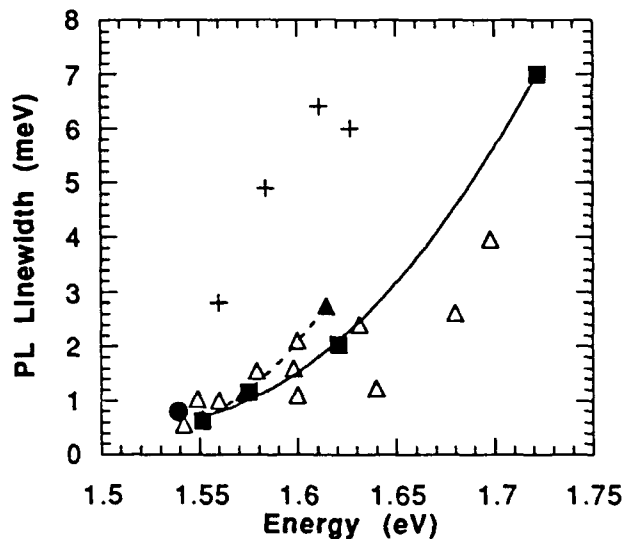MBE was 0.5 meV but for a 175Å well.

Figure 7   The reported best PL linewidths as a function of transition energies for single GaAs/ AlGaAs QWs
of different width. Plotted are QWs grown by (●) MOCVD, (+) CBE, (Δ) MBE. Our data for GSMBE growth (■ -
solid line) with interrupt at both interfaces and GSMBE (▲ -dotted line) with interrupt at only the normal interface (9)
are superimposed.

Laser Induced fluorescence

This section describes the methods used to obtain chemical species identification, concentration and
reaction rates by in-situ LIF during a GSMBE growth run. The first important task is to measure the sticking
coefficient of various group III elements and group V dimers in the GSMBE system by LIF. Experimentally the
determination of the group III atom sticking coefficient is much easier than for those of group V dimeric species.
The following describes some basic results that we have obtained in monitoring the group V dimeric P_2 species
and its concentration dependence versus temperature above an InP surface.

When LIF is used to measure flux intensity in the VG MBE chamber, both incident and reflected flux are
measured because of the Knudsen cell and substrate holder geometry. The total flux measurement can easily be
corrected for the offset of the incident flux and the time dependent reflected flux intensity can thus be obtained.

Since the substrate surface is at a constant temperature, the signal we monitor after the incident flux goes to zero (ie the MBE shutter is closed) is the isothermal desorption flux [10]. From this measurement , the desorption rate can be measured for the 100% coverage case and the correction for the sticking coefficient can be obtained.

Assuming a first order desorption, the desorption rate follows an Arrhenius behavior:

$$ k = v \exp \left(\frac{-E}{k_B T} \right) $$

where T is the substrate temperature, E is the energy barrier for the desorption, and v is the pre-exponential factor, which does not have as clear a physical interpretation as the one in gas phase. The energy barrier for desorption can thus be derived from the temperature dependent measurements of the desorption rate.

For the group V dimer flux, the measurements of sticking coefficient and desorption rate are more complicated than the group III element flux because of the molecular energy distribution among the many vibrational and rotational states. Fortunately, the internal energy stored in the vibrational and rotational states can also be quantified by LIF. Since LIF has the capability to monitor the dimer flux intensity for a particular rotational and vibrational state, we can in principle, measure the sticking coefficient and the desorption rate of different vibrational and rotational states. Any possible internal energy dependence of surface growth kinetics can thus be studied.

Initial experiments we performed investigated the thermal desorption of P_2 from the InP surface. The P_2 C-X(1,0) LIF spectrum and the calculated spectrum are shown in the top and bottom parts of figure 8, respectively. The calculated spectrum used the molecular constants given by Herzberg. There is good agreement in the position of the transitions between theory and experiment, indicating that the chemical species P_2 has been identified. The extra lines and energy level shift in the high J states are due to the perturbation of the C state by the nearby c state in a low J state. At low J states both line positions and intensities fit well with the calculations indicating a smaller perturbation. Also observed is that the P and R branch transitions are well separated. Because the C(v=1) state is not perturbed by the nearby c state, we can use the C(v=1) state to monitor the ground state population during MBE growth. This is in fact what we do.
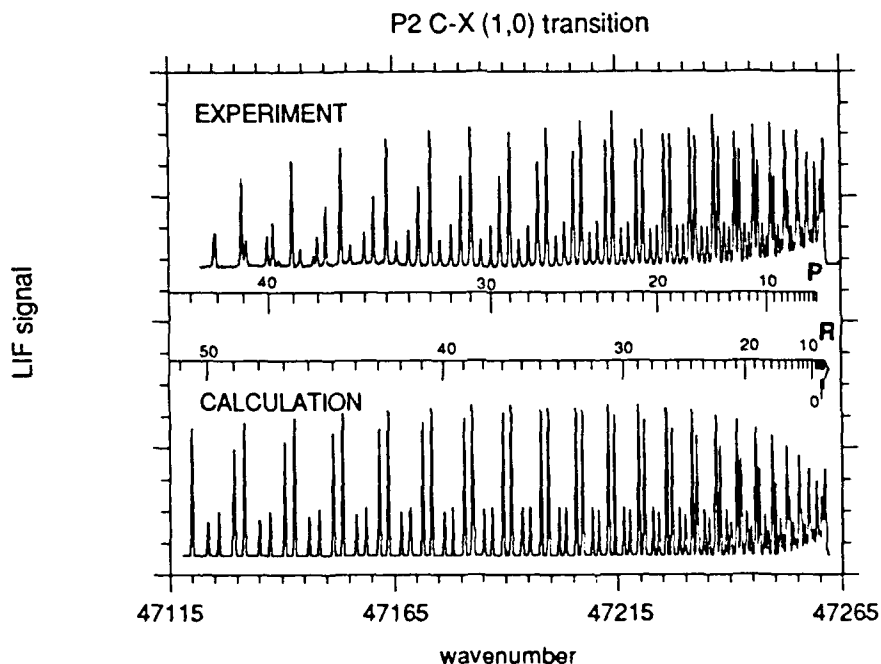

Figure 8   Measured (top) laser induced fluorescence spectrum of P_2 molecules desorbing from an InP substrate. The bottom curve is a simulated spectrum of the P_2 C-X(1,0) transition. Comparison of the two confirms that the desorbing species is actually P_2.

The P_2 C-X(2,0) transition is used to monitor the temperature dependence of P_2 desorption from the InP substrate. As shown in figure 9, there is a strong dependence of LIF intensity as a function of substrate temperature. The relative P_2 partial pressure is measured by integration of the first six peaks of the P_2 LIF spectrum. Because the vibrational and rotational state Boltzmann distributions are the same for the range of temperatures considered, the integral is directly proportional to the P_2 desorption rate. By normalizing the area to the measured 833K value, we obtain the relative P_2 pressure at different substrate temperatures.
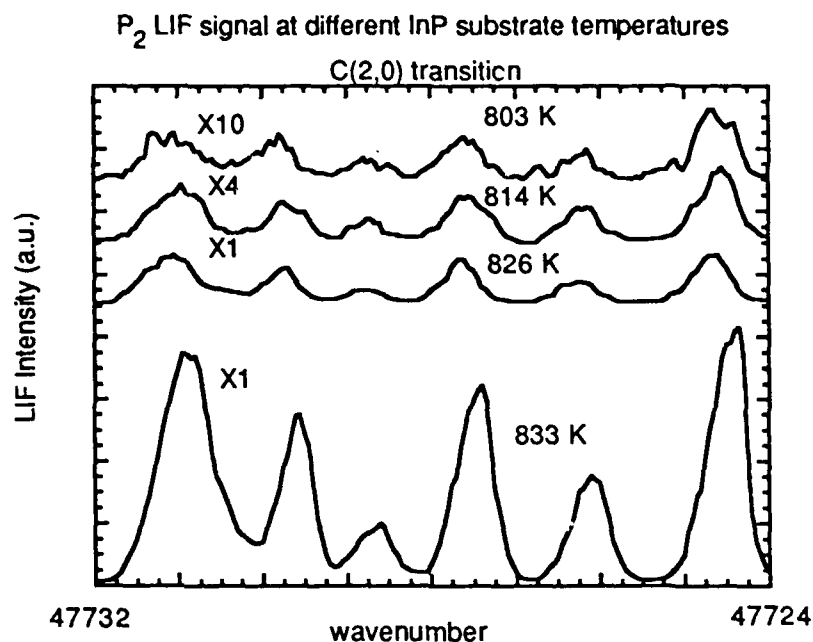
P₂ LIF signal at different InP substrate temperatures

C(2,0) transition

Figure 9   First six peaks of the P_2 C(2,0) transition as a function of temperature showing the thermal decomposition of an InP substrate. The integrated LIF signal is proportional to the partial pressure of the dimeric species.

The temperature dependent pressure from P_2 desorption can then be described by the simple equation
$\ln(P) = -A/T + B$
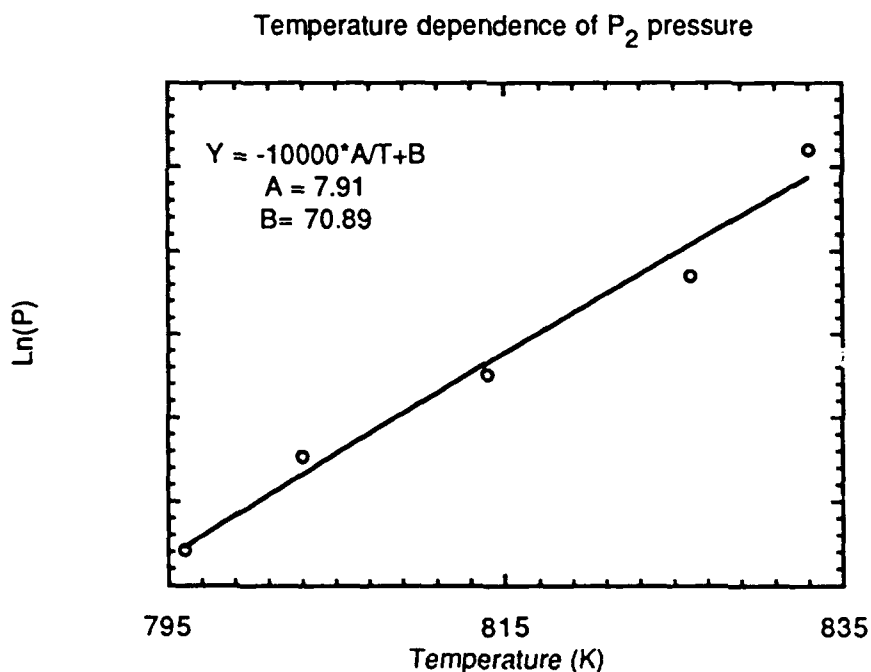as shown in figure 10. The measured pressure has the expected exponential temperature dependence.

Temperature dependence of P₂ pressure

Figure 10   Plot of the logarithm of P_2 pressure versus temperature taken from the LIF spectra. The exponential behavior is clearly indicated from the linear fit.

Monitoring of the LIF spectra of group III atoms is simpler because of the significantly smaller vibrational and rotational states. We have successfully monitored Ga and In using the LIF technique. An advantage of LIF over modulated beam mass spectrometry (MBMS) in measuring group III concentrations is that the LIF technique

lends itself to spatial probing of chemical species away from the growth surface thus facilitating the determination of absolute concentrations of incident and desorbing species.

Reflection high energy electron diffraction

The RHEED technique has been developed to a high degree so that it is routinely used to measure the growth rate and the structural properties of the surface. RHEED is used most commonly to detect oxide desorption from the GaAs surface. It is also used to calibrate the temperature measurements by locating the transition position (congruent sublimation temperature) of the GaAs surface from arsenic stable (2x4) to a Ga stable (4x2). It is also used to study surface step distributions [11-13] by observing splitting of the diffraction streaks. In dynamic studies, the oscillations in the RHEED intensity of the specular beam during growth was found to correspond to the growth of monolayers.

Sustained RHEED oscillations during GaAs growth over long periods of time during GSMBE growth is a clear evidence of layer-by-layer growth during GSMBE. These oscillations, apart from being useful for the evaluation of growth rate and composition, are also useful in determining the effects of transients during shutter operation. These oscillations show very little change in growth rate even after growth of tens of monolayers. Transients are a strong function of crucible design and although the crucibles being used have terrible nonuniformity [15], they show a good transient response unlike the recent high uniformity cells that exhibit excellent uniformity characteristics but very poor transient response. A beat frequency associated with the oscillations is observed and this is a result of the growth non-uniformity as seen by the large RHEED spot in the absence of substrate rotation.

We have studied the recovery time of the RHEED intensity as a function of quantum well thickness [14]. Extensive studies at normal and inverted interfaces with and without growth interruption for QW growth have been performed and some of the results are mentioned here. We observed that there is no significant change in recovery time at the normal interface as a function of QW thickness. Even at growth rates of about 1μm per hour, complete recovery is seen within about 20 sec. This shows that an interrupt of 20 sec. at the normal interface provides adequate time for the completion of the monolayer and removal of excess Ga as suggested in the theory. As the growth temperature increases, the recovery becomes faster. This is due to the increased migration of atoms forming complete layers quickly. Below about 640°C, there is no significant change in oscillation period as a result of a constant growth rate.

A comparison of recovery of the RHEED intensity for growth with As_2 and As_4 at approximately 580°C has been performed. At low temperatures the intensity recovers quickly in the case of As_4, but never completely. Inability to recover to the original intensity indicates a small roughness which could be due to an incomplete layer that results with As_4 growth. However over long interrupt times, the intensity recovers to the initial value. In case of As_2, the recovery is complete and the intensity reaches the original starting intensity steadily, although the initial rise is slower as compared to As_4 growth. This result is attributed to the more efficient surface growth kinetics of As_2 and the contribution of hydrogen toward forming complete layers. The intensity at higher temperatures rises above the starting intensity. At higher temperatures the surface steadily gets rougher due to Ga desorption, resulting in a small decrease in intensity to begin with. However, immediately after growth, the surface is smooth again and longer interruption times at high temperatures slowly degrades the surface. Additional arsenic is needed to keep the surface stable above 640°C. During growth, the arsenic to gallium atom ratio is approximately 1.4. With As_4, this number is doubled since the incorporation efficiency is, at the best only 50%. The exact ratio of atoms is determined by arsenic induced oscillations. At the inverted interface, recovery time is affected by the percentage of aluminum present in the layers. At higher Al composition and at temperatures less than 620°C, the surface does not recover completely even after long interrupt times, indicating inability of Al atoms to migrate and form complete layers. The recovery of AlGaAs for composition of 0.3 that is commonly used, is very similar to the GaAs surface. In contrast, AlAs growth shows a recovery of RHEED intensity at temperatures only above 660°C.

Molecular hydrogen was used to study its effects on GaAs growth in the cracker cell kept at 1000°C. No clear change in RHEED reconstructions were noticed even after extensive studies. Partial pressure of the added hydrogen was 1.5×10^{-5} mbar as measured from the BMIG. There is abundant hydrogen obtained from the cracking of arsine and hence the effect of additional hydrogen is relatively small. This however, was sufficient to cause a 4% decrease in growth rate as seen from the change in RHEED oscillations. Experiments with a gradual increase in hydrogen flow showed a corresponding decrease in growth rate. Hydrogen thus affects both Ga and As incorporation; but it has not been possible to obtain quantitative results. It is well known that in MBE, a surface above CST, in the absence of arsenic flux shows a Ga stable (4x2) reconstruction and below CST, an arsenic stable pattern is seen. However, in GSMBE, in the presence of residual hydrogen, even at temperatures as low as 580°C, the surface slowly turns to a Ga stable (1x3) or (4x2) in the absence of arsenic flux, indicating a slow removal process for arsenic covering the surface. At temperatures below 600°C, in the absence of hydrogen and arsenic, a Ga pre-deposited surface slowly changes from (4x2) to (2x4). In contrast, in GSMBE where there is a large quantity of residual hydrogen, the surface does not show any signs of change in reconstruction unless and until arsenic flux is turned on. These two observations, along with the reported GaAs etching results indicate a removal of arsenic and Ga atoms from the GaAs surface. Thus, hydrogen displaced arsenic is replaced by the arsenic over pressure and, free Ga is affected by hydrogen helps create an atomically sharp interface.

The observations justify the theoretically predicted model for growth kinetics with As$_2$ and hydrogen. The studies just mentioned enabled the determination of exact conditions for obtaining smooth interfaces with GSMBE growth.

Our recent studies include RHEED observations of InP growth on GaAs substrate. The initial island formation and the occurrence of 3D growth with the deposition of InP monolayers have been monitored. We have tracked the evolution of the RHEED patterns along the [1$\bar{1}$0] direction after 1, 4 and 16 MLs of InP deposition on a GaAs substrate. We find that after the deposition of approximately 4 MLs of InP, island growth occurs. Islands have sloping <113> sides oriented along the [1$\bar{1}$0] direction and are starting to merge after the deposition of approximately 16 MLs. The effects of substrate temperature are also being studied.

Summary

We have demonstrated a multifaceted approach to measuring growth processes in gas source MBE. This includes the development and implementation of in-situ growth monitoring techniques that characterize optical, chemical and structural properties of the growing epitaxial layers. Our laboratory is unique in that these analyses can be combined to produce information for growth models. Using these methods, we have obtained record quantum well PL linewidths, observed interface smoothing at heterojunctions by ellipsometry, identified the atomic and dimeric chemical species above the growing surface, extended the range of substrate temperature determination from 400°C down to room temperature and tracked the growth of quantum wells by optical techniques. The information obtained will be used by our group and others to model the growth of semiconductor materials and heterojunction interfaces.

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Figure captions

Figure 1   A comparison of substrate temperature determined by thermocouple, optical pyrometer and spectroscopic ellipsometer. The difference between the thermocouple and ellipsometer is plotted on the axes to the right. It should be noted that the ellipsometer can measure temperature from typical growth temperatures to room temperature.

Figure 2   Real-time monitoring by of the growth of a thick (2500Å) AlGaAs epitaxial layer on a GaAs substrate. This curve was taken at a wavelength of 5000Å.

Figure 3   At higher time resolution, the behavior of psi is measured after the Ga smoothing pulse is turned off. The data (solid line) is fit with an exponential (dashed line) yielding a time constant of approximately 80 seconds.

Figure 4   The velocity plot corresponding to the growth run shown in figure 2 shows the spiraling of the trajectory to the optically thick values of GaAs and AlGaAs at the wavelength of 5000Å.

Figure 5   Ellipsometric tracking of the growth of a 20 period MBE AlGaAs/GaAs multiple quantum well.

Figure 6   2K PL linewidths are plotted for 50Å, 75Å and 100Å GaAs/ AlGaAs QWs grown at different substrate temperatures. All QWs were grown with only one interrupt at the normal interface except for the QWs grown at 626°C which had interrupts both at the normal and inverted interfaces. The 2K linewidth for the 100Å GSMBE well is 0.62 meV which is close to the best obtained solid source MBE value of 0.5 meV.

Figure 7   The reported best PL linewidths as a function of transition energies for single GaAs/ AlGaAs QWs of different width. Plotted are QWs grown by (●) MOCVD, (+) CBE, (Δ) MBE. Our data for GSMBE growth (■ - solid line) with interrupt at both interfaces and GSMBE (▲ -dotted line) with interrupt at only the normal interface (9) are superimposed.

Figure 8   Measured (top) laser induced fluorescence spectrum of P_2 molecules desorbing from an InP substrate. The bottom curve is a simulated spectrum of the P_2 C-X(1,0) transition. Comparison of the two confirms that the desorbing species is actually P_2.

Figure 9   First six peaks of the P_2 C(2,0) transition as a function of temperature showing the thermal decomposition of an InP substrate. The integrated LIF signal is proportional to the partial pressure of the dimeric species.

Figure 10   Plot of the logarithm of P_2 pressure versus temperature taken from the LIF spectra. The exponential behavior is clearly indicated from the linear fit.